14.2: The First Law of Thermodynamics
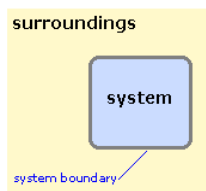
> ### 🧠 Learning Objectives
>
> Make sure you thoroughly understand the following essential concepts:
>
> - Define: *system*, *surroundings*, *state properties*, *change of state* (how the latter is calculated).
> - Write out the equation that defines the *First Law*, and explain its physical meaning.
> - Describe the meaning of a *pathway* in thermodynamics, and how it relates to *state functions*.
> - Comment on the meaning of *pressure-volume work*: how is it calculated? What kinds of chemical reactions involve *P-V* work?
> - Define *isothermal* and *adiabatic* processes, and give examples of each.
> - Using the expansion of a gas as an example, state the fundamental distinction between *reversible* and irreversible changes in terms of the system + surroundings.
> - Explain how *enthalpy change* relates to *internal energy*, and how it can be observed experimentally.
> - Define *heat capacity*; explain its physical significance, and why there is a difference between C_p and C_v.

"Energy cannot be created or destroyed"— this fundamental law of nature, more properly known as **conservation of energy**, is familiar to anyone who has studied science. Under its more formal name of the *First Law of Thermodynamics*, it governs all aspects of energy in science and engineering applications. It's special importance in Chemistry arises from the fact that virtually all chemical reactions are accompanied by the uptake or release of energy. One of the interesting things about thermodynamics is that although it deals with matter, it makes no assumptions about the microscopic nature of that matter. Thermodynamics deals with matter in a macroscopic sense; it would be valid even if the atomic theory of matter were wrong. This is an important quality, because it means that reasoning based on thermodynamics is unlikely to require alteration as new facts about atomic structure and atomic interactions come to light.

A Thermodynamic view of the world

In thermodynamics, we must be very precise in our use of certain words. The two most important of these are *system* and *surroundings*. A *thermodynamic system* is that part of the world to which we are directing our attention. Everything that is not a part of the system constitutes the *surroundings*. The system and surroundings are separated by a *boundary*.

If our system is one mole of a gas in a container, then the boundary is simply the inner wall of the container itself. The boundary need not be a physical barrier; for example, if our system is a factory or a forest, then the boundary can be wherever we wish to define it. We can even focus our attention on the dissolved ions in an aqueous solution of a salt, leaving the water molecules as part of the surroundings. The single property that the boundary must have is that it be clearly defined, so we can unambiguously say whether a given part of the world is in our system or in the surroundings.

> *If matter is not able to pass across the boundary, then the system is said to be closed; otherwise, it is open. A closed system may still exchange energy with the surroundings unless the system is an isolated one, in which case neither matter nor energy can pass across the boundary. The tea in a closed Thermos bottle approximates a closed system over a short time interval.*

The *properties* of a system are those quantities such as the pressure, volume, temperature, and its composition, which are in principle measurable and capable of assuming definite values. There are of course many properties other than those mentioned above; the density and thermal conductivity are two examples. However, the pressure, volume, and temperature have special

significance because they determine the values of all the other properties; they are therefore known as *state properties* because if their values are known then the system is in a definite *state*.

In dealing with thermodynamics, we must be able to unambiguously define the change in the state of a system when it undergoes some process. This is done by specifying changes in the values of the different state properties using the symbol Δ (*delta*) as illustrated here for a change in the volume:

$$\Delta V = V_{final} - V_{initial} \tag{14.2.1}$$

We can compute similar delta-values for changes in *P*, *V*, n_i (the number of moles of component *i*), and the other state properties we will meet later.

Internal energy is simply the totality of all forms of kinetic and potential energy of the system. Thermodynamics makes no distinction between these two forms of energy and it does not assume the existence of atoms and molecules. But since we are studying thermodynamics in the context of chemistry, we can allow ourselves to depart from "pure" thermodynamics enough to point out that the internal energy is the sum of the kinetic energy of motion of the molecules, and the potential energy represented by the chemical bonds between the atoms and any other intermolecular forces that may be operative.

How can we know how much internal energy a system possesses? The answer is that we cannot, at least not on an absolute basis; all scales of energy are arbitrary. The best we can do is measure changes in energy. However, we are perfectly free to define zero energy as the energy of the system in some arbitrary *reference state*, and then say that the internal energy of the system in any other state is the difference between the energies of the system in these two different states.

The First Law of Thermodynamics

This law is one of the most fundamental principles of the physical world. Also known as the *Law of Conservation of Energy*, it states that energy can not be created or destroyed; it can only be redistributed or changed from one form to another. A way of expressing this law that is generally more useful in Chemistry is that any change in the internal energy of a system is given by the sum of the heat *q* that flows across its boundaries and the work *w* done on the system by the surroundings.
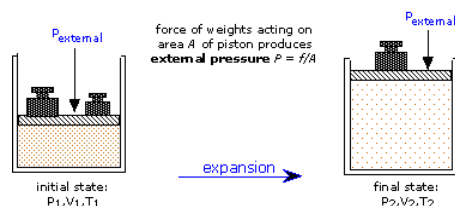
$$\Delta U = q + w \tag{14.2.2}$$

This says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the world outside the system- in other words, energy cannot be created or destroyed.

There is an important **sign convention** for heat and work that you are expected to know. If heat flows into a system or the surroundings to do work on it, the internal energy increases and the sign of *q* or *w* is positive. Conversely, heat flow out of the system or work done by the system will be at the expense of the internal energy, and will therefore be negative. (Note that this is the opposite of the sign convention that was commonly used in much of the pre-1970 literature.) The full significance of Equation 14.2.2 cannot be grasped without understanding that *U* is a *state function*. This means that a given change in internal energy Δ*U* can follow an infinite variety of *pathways* corresponding to all the possible combinations of *q* and *w* that can add up to a given value of Δ*U*.

As a simple example of how this principle can simplify our understanding of change, consider two identical containers of water initially at the same temperature. We place a flame under one until its temperature has risen by 1°C. The water in the other container is stirred vigorously until its temperature has increased by the same amount. There is now no physical test by which you could determine which sample of water was warmed by performing work on it, by allowing heat to flow into it, or by some combination of the two processes. In other words, there is no basis for saying that one sample of water now contains more "work", and the other more "heat". The only thing we can know for certain is that both samples have undergone identical increases in internal energy, and we can determine the value of simply by measuring the increase in the temperature of the water.

Pressure-volume work

The kind of work most frequently associated with chemical change occurs when the volume of the system changes owing to the disappearance or formation of gaseous substances. This is sometimes called expansion work or *PV*-work, and it can most easily be understood by reference to the simplest form of matter we can deal with, the hypothetical *ideal gas*.

force of weights acting on
area *A* of piston produces
external pressure *P* = *f*/*A*

initial state:
P_1, V_1, T_1

expansion

final state:
P_2, V_2, T_2

The figure shows a quantity of gas confined in a cylinder by means of a moveable piston. Weights placed on top of the piston exert a force f over the cross-section area *A*, producing a pressure $P = f / A$ which is exactly countered by the pressure of the gas, so that the piston remains stationary. Now suppose that we heat the gas slightly; according to Charles' law, this will cause the gas to expand, so the piston will be forced upward by a distance Δx. Since this motion is opposed by the force f, a quantity of work $f \, \Delta x$ will be done by the gas on the piston. By convention, work done by the system (in this case, the gas) on the surroundings is negative, so the work is given by

$$w = - f\Delta x \tag{14.2.3}$$

When dealing with a gas, it is convenient to think in terms of the more relevant quantities pressure and volume rather than force and distance. We can accomplish this by multiplying the second term by *A/A* which of course leaves it unchanged:

$$w = -f\Delta x \frac{A}{A} \tag{14.2.4}$$

By grouping the terms differently, but still not changing anything, we obtain

$$w = -\frac{f}{A}\Delta x A \tag{14.2.5}$$

Since pressure is force per unit area and the product of the length *A* and the area has the dimensions of volume, this expression becomes

$$w = - P\Delta V \tag{14.2.6}$$

It is important to note that although P and V are state functions, the *work* is not (that's why we denote it by a lower-case *w*.) As is shown farther below, the quantity of work done will depend on whether the same net volume change is realized in a single step (by setting the external pressure to the final pressure P), or in multiple stages by adjusting the restraining pressure on the gas to successively smaller values approaching the final value of P.

> ✔ **Example 14.2.1**
>
> Find the amount of work done on the surroundings when 1 liter of an ideal gas, initially at a pressure of 10 atm, is allowed to expand at constant temperature to 10 liters by:
>
> a. reducing the external pressure to 1 atm in a single step,
> b. reducing P first to 5 atm, and then to 1 atm,
> c. allowing the gas to expand into an evacuated space so its total volume is 10 liters.
>
> ***Solution***
>
> First, note that ΔV, which is a state function, is the same for each path:
>
> $$V_2 = (10/1) \times (1L) = 10L \tag{14.2.7}$$
>
> so
>
> $$\Delta V = 9 \ L \tag{14.2.8}$$
>
> For path *(a)*
>
> $$w = -(1 \text{ atm}) \times (9 \text{ L}) = \textbf{–9 L-atm}.$$
>
> For path *(b)*, the work is calculated for each stage separately:
>
> $$w = -(5 \text{ atm}) \times (2–1 \text{ L}) - (1 \text{ atm}) \times (10–2 \text{ L}) = \textbf{–13 L-atm}$$

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For path *(c)* the process would be carried out by removing all weights from the piston in Figure 14.2.1 so that the gas expands to 10 L against zero external pressure. In this case *w* = (0 atm) × 9 L = **0**; that is, *no work is done because there is no force to oppose the expansion.*

Adiabatic and Isothermal Processes

When a gas expands, it does work on the surroundings; compression of a gas to a smaller volume similarly requires that the surroundings perform work on the gas. If the gas is thermally isolated from the surroundings, then the process is said to occur *adiabatically*. In an adiabatic change, *q* = 0, so the First Law becomes Δ*U* = 0 + *w*. Since the temperature of the gas changes with its internal energy, it follows that adiabatic compression of a gas will cause it to warm up, while adiabatic expansion will result in cooling.

In contrast to this, consider a gas that is allowed to slowly escape from a container immersed in a constant-temperature bath. As the gas expands, it does work on the surroundings and therefore tends to cool, but the thermal gradient that results causes heat to pass into the gas from the surroundings to exactly compensate for this change. This is called an *isothermal* expansion. In an isothermal process the internal energy remains constant and we can write the First Law (Equation $Ref2-1$) as

$$0 = q + w \tag{14.2.9}$$

or

$$q = -w \tag{14.2.10}$$

This illustrates that the heat flow and work done exactly balance each other.

Because no thermal insulation is perfect, truly adiabatic processes do not occur. However, heat flow does take time, so a compression or expansion that occurs more rapidly than thermal equilibration can be considered adiabatic for practical purposes. If you have ever used a hand pump to inflate a bicycle tire, you may have noticed that the bottom of the pump barrel can get quite warm. Although a small part of this warming may be due to friction, it is mostly a result of the work you (the surroundings) are doing on the system (the gas.)

Adiabatic expansion and contractions are especially important in understanding the behavior of the **atmosphere**. Although we commonly think of the atmosphere as homogeneous, it is really not, due largely to uneven heating and cooling over localized areas. Because mixing and heat transfer between adjoining parcels of air does not occur rapidly, many common atmospheric phenomena can be considered at least quasi-adiabatic.

Reversible processes

From Example 14.2.1 we see that when a gas expands into a vacuum ($P_{external} = 0$ the work done is zero. This is the *minimum work* the gas can do; what is the *maximum work* the gas can perform on the surroundings? To answer this, notice that more work is done when the process is carried out in two stages than in one stage; a simple calculation will show that even more work can be obtained by increasing the number of stages— that is, by allowing the gas to expand against a series of successively lower external pressures. In order to extract the maximum possible work from the process, the expansion would have to be carried out in an infinite sequence of infinitesimal steps. Each step yields an increment of work *P* Δ*V* which can be expressed as (*RT/V*) *dV* and integrated:

$$w = \int_{V_1}^{V_2} \frac{RT}{V} dv \tag{14.2.11}$$

$$= RT \ln \frac{V_2}{V_1} \tag{14.2.12}$$

Although such a path (which corresponds to what is called a *reversible process*) cannot be realized in practice, it can be approximated as closely as desired.

Even though no real process can take place reversibly (it would take an infinitely long time!), reversible processes play an essential role in thermodynamics. The main reason for this is that q_{rev} and w_{rev} are *state functions* which are important and are easily calculated. Moreover, many real processes take place sufficiently gradually that they can be treated as approximately reversible processes for easier calculation.
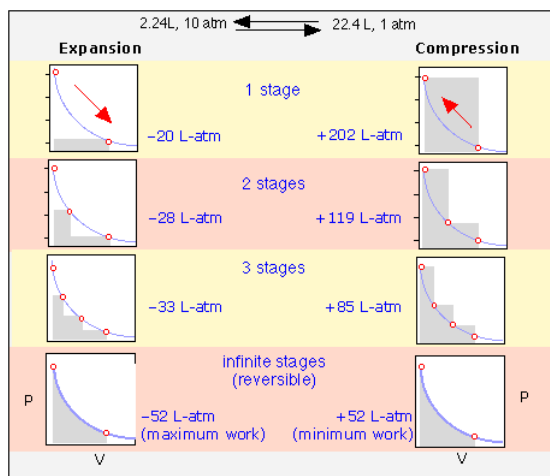
Figure 14.2.1: These plots illustrate the effects of various degrees of reversibility on the amount of work done when a gas expands, and the work that must be done in order to restore it to its initial state by recompressing it. The work, in each case, is proportional to the shaded area on the plot.

Each expansion-compression cycle leaves the gas unchanged, but in all but the one in the bottom row, the surroundings are forever altered, having expended more work in compressing the gas than was performed on it when the gas expanded. Only when the processes are carried out in an *infinite* number of steps will the system *and* the surroundings be restored to their initial states— this is the meaning of thermodynamic reversibility.

Heat changes at constant pressure: the Enthalpy

For a chemical reaction that performs no work on the surroundings, the heat absorbed is the same as the change in internal energy: $q = \Delta U$. But many chemical processes do involve work in one form or another:

- If the total volume of the reaction products exceeds that of the reactants, then the process performs work on the surroundings in the amount $P\Delta V$, in which P is the pressure exerted by the surroundings (usually the atmosphere) on the system.
- A reaction that drives an electrical current through an external circuit performs *electrical work* on the surroundings.

For an isothermal process, pressure-volume work affects the heat q

We will consider only pressure-volume work in this lesson. If the process takes place at a constant pressure, then the work is given by $P\Delta V$ and the change in internal energy will be

$$\Delta U = q - P\Delta V \tag{14.2.13}$$

Bear in mind why q is so important: the heat flow into or out of the system is directly measurable. ΔU, being "internal" to the system, is not directly observable. Thus the amount of heat that passes between the system and the surroundings is given by

$$q = \Delta U + P\Delta V \tag{14.2.14}$$

This means that if an exothermic reaction is accompanied by a net increase in volume under conditons of constant pressure, some heat additional to ΔU must be absorbed in order to supply the energy expended as work done on the surroundings if the temperature is to remain unchanged *(isothermal* process.)

For most practical purposes, changes in the volume of the system are only significant if the reaction is accompanied by a difference in the moles of gaseous reactants and products.

For example, in the reaction $H_2(g) + O_2(g) \rightarrow \frac{1}{2}H_2O(l)$, the total volume of the system decreases from that correponding to 2 moles of gaseous reactants to 0.5 mol of liquid water which occupies only 9 mL — a volume so small in comparison to that of the reactants that it can be neglected without significant error. So all we are really concerned with is the difference in the number of moles of gas Δn_g:

$\Delta n_g = (0 - 2)$ mol $= -2$ mol

This corresponds to a net contraction (negative expansion) of the system, meaning that the surroundings perform work on the system.

The molar volume of an ideal gas at 25° C and 1 atm is

(298/273) × (22.4 L mol⁻¹) = 24.5 L mol⁻¹

Remember the sign convention: a flow of heat or performance of work that supplies energy is positive; if it consumes energy, it is negative. Thus work performed by the surroundings diminishes the energy of the surroundings ($w_{surr} < 0$) and increases the energy of the system ($w_{sys} > 0$).

and the work done (by the surroundings on the system) is

(1 atm) (–2 mol)(24.5 L mol⁻¹) = –49.0 L-atm.

Using the conversion factor 1 J = 101.3 J, and bearing in mind that work performed *on* the system supplies energy *to* the system, the work associated solely with the volume change of the system increases its energy by

(101.3 J/L-atm)(–49.0 L-atm) = 4964 J = 4.06 kJ

> ✔ Example 14.2.2
>
> The above reaction $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ is carried out at a constant pressure of 1 atm and a constant temperature of 25° C. What quantity of heat q will cross the system boundary (and in which direction?) For this reaction, the change in internal energy is $\Delta U = -281.8$ kJ/mol.
>
> **Solution**
> 281.8 kJ of heat. The work performed by the surroundings supplies an additional energy of $P\,\Delta V = 4.06$ kJ to the system. The total energy change of the system is thus
>
> $q = (-281.8 + 4.06)$ k J = –285.8 kJ
>
> (Eq. 4.2 above.) In order to maintain the constant 25° temperature, an equivalent quantity of heat must pass from the system to the surroundings.

This terminology can be somewhat misleading unless you bear in mind that the conditions ΔP and ΔT refer to the differences between the *inital* and *final* states of the system — that is, *before* and *after* the reaction. During the time the reaction is in progress, the temperature of the mixture will rise or fall, depending on whether the process is exothermic or endothermic. But because ΔT is a state function, its value is independent of what happens "in between" the initial state (reactants) and final state (products). The same is true of ΔV.

> ## Enthalpy hides work and saves it too!

Because most chemical changes we deal with take place at constant pressure, it would be tedious to have to explicitly deal with the pressure-volume work details that were described above. Fortunately, chemists have found a way around this; they have simply defined a new state function that incorporates and thus hides within itself any terms relating to incidental kinds of work (*P-V*, electrical, etc.). Since both ΔP and ΔV in Equation 14.2.14 are state functions, then q_P, the heat that is absorbed or released when a process takes place at constant pressure, must also be a state function and is known as the *enthalpy change ΔH*

$$\Delta H \equiv q_P = \Delta U + P\Delta V \qquad (14.2.15)$$

Since most processes that occur in the laboratory, on the surface of the earth, and in organisms do so under a constant pressure of one atmosphere, Equation 14.2.15 is the form of the First Law that is of greatest interest to most of us most of the time.

> ✔ Example 14.2.3
>
> Hydrogen chloride gas readily dissolves in water, releasing 75.3 kJ/mol of heat in the process. If one mole of HCl at 298 K and 1 atm pressure occupies 24.5 liters, find ΔU for the system when one mole of HCl dissolves in water under these conditions.
>
> *Solution*
>
> In this process the volume of liquid remains practically unchanged, so $\Delta V = -24.5$ L. The work done is

$$w = -P\Delta V$$
$$= -(1\ atm)(-24.5\ L)$$
$$= 24.6\ L - atm$$

(The work is positive because it is being done on the system as its volume decreases due to the dissolution of the gas into the much smaller volume of the solution.) Using the conversion factor 1 L-atm = 101.33 J mol^{-1} and substituting in Equation 14.2.15 we obtain

$$\Delta U = q + P\Delta V$$
$$= -(75,300\ J) + [101.33\ J/L - atm)(24.5\ L - atm)]$$
$$= -72.82\ kJ$$

In other words, if the gaseous HCl could dissolve without volume change, the heat released by the process (75.3 kJ) would cause the system's internal energy to diminish by 75.3 kJ. But the disappearance of the gaseous phase reduces the volume of the system. This is equivalent to compression of the system by the pressure of the atmosphere performing work on it and consuming part of the energy that would otherwise be liberated, reducing the net value of ΔU to **–72.82 kJ**.

The Heat Capacity

For systems in which no change in composition (chemical reaction) occurs, things are even simpler: to a very good approximation, the enthalpy depends only on the temperature. This means that the temperature of such a system can serve as a direct measure of its enthalpy. The functional relation between the internal energy and the temperature is given by the *heat capacity* measured at constant pressure:

$$c_p = \frac{dH}{dT} \tag{14.2.16}$$

(or $\Delta H/\Delta T$ over a finite duration) An analogous quantity relates the heat capacity at constant *volume* to the internal energy:

$$c_v = \frac{dU}{dT} \tag{14.2.17}$$

The greater the heat capacity of a substance, the smaller will be the effect of a given absorption or loss of heat on its temperature. Heat capacity can be expressed in joules or calories per mole per degree (molar heat capacity), or in joules or calories per gram per degree; the latter is called the specific heat capacity or just the specific heat. The difference between c_p and c_v is of importance only when the volume of the system changes significantly— that is, when different numbers of moles of gases appear on either side of the chemical equation. For reactions involving only liquids and solids, c_p and c_v are for all practical purposes identical.

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